Alkyd–Epoxy Blends as Multipurpose Coatings

N. Dutta, N. Karak, S. K. Dolui

Department of Chemical Sciences, Tezpur University, Napaam, Tezpur 784028, Assam, India

ABSTRACT: The alkyd resins of three different compositions based on nahar seed oil (*Mesua ferrea*), phthalic anhydride, and maleic anhydride were synthesized by an alcoholysis method. These alkyd resins were blended with a commercially available epoxy resin (Araldite 250, Ciba Geigy, Mumbai, India) separately to study the performance of the blends as coatings. The morphology of the blends was studied with scanning electron microscopy. The drying time, gloss, flexibility, pencil hardness, adhesion, pressure test, and chemical resistance under different conditions were measured for this purpose. The thermal characteristics of the blends were also investigated by thermogravimetric analysis. The studies showed better performance of the blends with respect to the drying time, hardness, flexibility, gloss, pressure test, thermal stability, and chemical resistance. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 516–521, 2006

Key words: blends; coatings; resins

INTRODUCTION

Alkyd-based coatings find uses in a large variety of applications, such as architectural and industrial finishes and industrial maintenance.[1] Alkyd resins play important roles as coating binders,[2] mainly for two reasons. First, alkyds are extremely versatile with respect to their structures and properties, as they can be synthesized from a variety of natural raw materials; second, the overall cost is low.[3–6] However, they suffer from some major problems, such as low alkali resistance, long drying times (prepared specially from nondrying oils), moderate adhesion, and low hardness. As alkyd resins have good compatibility with a wide variety of other coating resins,[7] such as nitrocellulose, amino resins, synthetic latex paints, and silicone resins, the aforementioned properties can be improved via blending with other suitable resins.

Epoxy resins have been commercially available for more than 50 years and find uses in a diverse range of applications, especially in the adhesive and surface coating industry.[8] They possess better adhesion, alkali and water resistance, thermal stability, mechanical properties, drying times, and so forth than alkyd resins but have inferior acid resistance, gloss, and so forth. Blending techniques may be used effectively to improve the inferior properties of both resins. Miscible polymer blends produce a new improved material from less superior individual components, but well-established miscible polymer blends are very rarely obtained.[9,10] However, immiscible or semimiscible blends with highly disperse mixtures also improve properties to an acceptable range.[11] There are reports and patents on the improvement of coating properties of alkyd resins via blending with other resins.[12–15] We have synthesized an alkyd resin based on nahar seed oil,[16] which is available in the north-east region. To modify the properties of the alkyd based on nahar seed oil, we attempted to blend it with epoxy. This article reports the coating performance characteristics of the alkyd based on nahar seed oil and epoxy resin blends as low-cost, multipurpose coatings.

EXPERIMENTAL

Materials and preparation of the samples

Nahar seed (Barpeta, Assam, India), used for the collection of oil, phthalic anhydride (PA), maleic anhydride (MA), glycerol, and lead monoxide (S.D. Fine Chemical, Ltd., Mumbai, India) were used without further purification. Araldite LY 250, a hardener (Hindustan Ciba Geigy, Ltd.), was used as received.

Alkyd resins of three different compositions with nahar seed oil, glycerol, PA, and MA, via an alchoholysis technique, with PbO as a catalyst were prepared on the basis of our earlier work.[16] The compositions of the alkyd resins along with important characteristics are shown in Table I.

A bisphenol A based epoxy resin, modified with a reactive diluent, and a polyamidoamine-based hardener were used. Specifications for the epoxy resin and hardener are given in Table II.

Correspondence to: N. Karak (nkarak@tezu.ernet.in).

TABLE I
Compositions and Properties of the Alkyd Resins

Resin	Amount of anhydride	AV (mg of KOH/g)	IV (g of I$_2$/100g)	SV (mg of KOH/g)	Viscosity (kP)[a]
Resin A (R-1)	100% PA	18.61	56.47	353.53	20
Resin B (R-2)	50% PA + 50% MA	23.68	50.72	377.60	50
Resin C (R-3)	25% PA with 75% MA	34.00	57.21	295.02	45

AV = acid value; IV = iodine value; SV = saponification value.
[a] Brookfield viscometer; spindle no. 4; speed = 0.6 rpm at 28°C.

Preparation of the blends

The blends of alkyd and epoxy resins were prepared by a solution technique with a 50 : 50 (w/w) benzene/petroleum ether solvent mixture. The alkyd and epoxy resins were separately thinned to a 50% solid content and then mixed together along with the hardener. The hardener was added in each case, with the ratio of the epoxy to the hardener kept at 2 : 1. The compositions of the blends are shown in Table III.

Instruments and test methods

The morphology of the blends was studied by scanning electron microscopy (SEM) analysis with a JSM 35CF (JEOL, Peabody, MA) after gold coating. The thermogravimetric analysis (TGA) of the blends was performed with a Mettler–Toledo (Columbus, OH) TGA analyzer/SDTA 821^e under an N$_2$ atmosphere at a heating rate of 10°C/min. Fourier transform infrared (FTIR) spectra of the films of cured resins and blends were recorded with a Nicolet (Madison, WI) 410 FTIR instrument.

The flexibility was tested with a mandrel tester. A resin-coated tin panel (100 mm × 50 mm × 0.315 mm) was bent over a 6.25-mm-diameter mandrel through 180° and examined for any damage, detachment, or cracking of the film according to the standard procedure.[17] The gloss characteristics of the blends were determined with a glossometer over a resin-coated mild steel panel (100 mm × 50 mm × 0.315 mm) at an angle of incidence of 60°.[18] A pressure test was performed with a pressure of 1.81 kg kept over the tested film for 5 min with the standard test method.[19] The

mild steel panels were coated with the blends and allowed to dry at a particular temperature and time recorded for hard dryness of the film. The blends were uniformly coated on the mild steel panels and kept for 7 days for maturation after curing, and then a hardness test was performed with lead pencils graded from 6B to 6H with the standard test method.[20] The adhesion performance of the blends and the individual resin was tested with commercial cello tape according to the cross-cut adhesion test method (ASTM D 3359). The chemical resistance of the cured resin blends coated on glass plates was tested according to ASTM D 593-67.[21]

RESULTS AND DISCUSSION

Blending morphology

The ability to produce blends with an improved combination of properties of the individual components depends on the degree of compatibility of the system. Alkyd resins in general show good compatibility with epoxy resins in industrially used solvents. However, two or more distinct layers may be formed, depending on the number of incompatible ingredients present in the blends.[22] Even two miscible polymers may form a two-phase mixture when dissolved in certain solvents. Therefore, a large variety of combinations of solvents were tested to achieve the desired solvent compatibility, evaporation rate, and ultimately uniform phase formation. A solvent system consisting of an equal weight mixture of benzene and petroleum ether was best and showed a clear single-phase solution. Hence, that solvent mixture was used to prepare the blends throughout this study.

TABLE II
Specifications of the Epoxy Resin and Hardener

Name	Araldite LY 250 (Ciba Geigy)	Hardener HY 840 (Ciba Geigy)
Viscosity at 25°C (mPa s)	450–650	10,000–25,000
Epoxy equivalent (g/equiv)	182–192	—
Epoxy content (equiv/kg)	5.2–5.5	—
Amine value (equiv/kg)	—	6.6–7.5
Density at 25°C (g/cm^3)	1.15	0.98

TABLE III
Recipes of the Blends

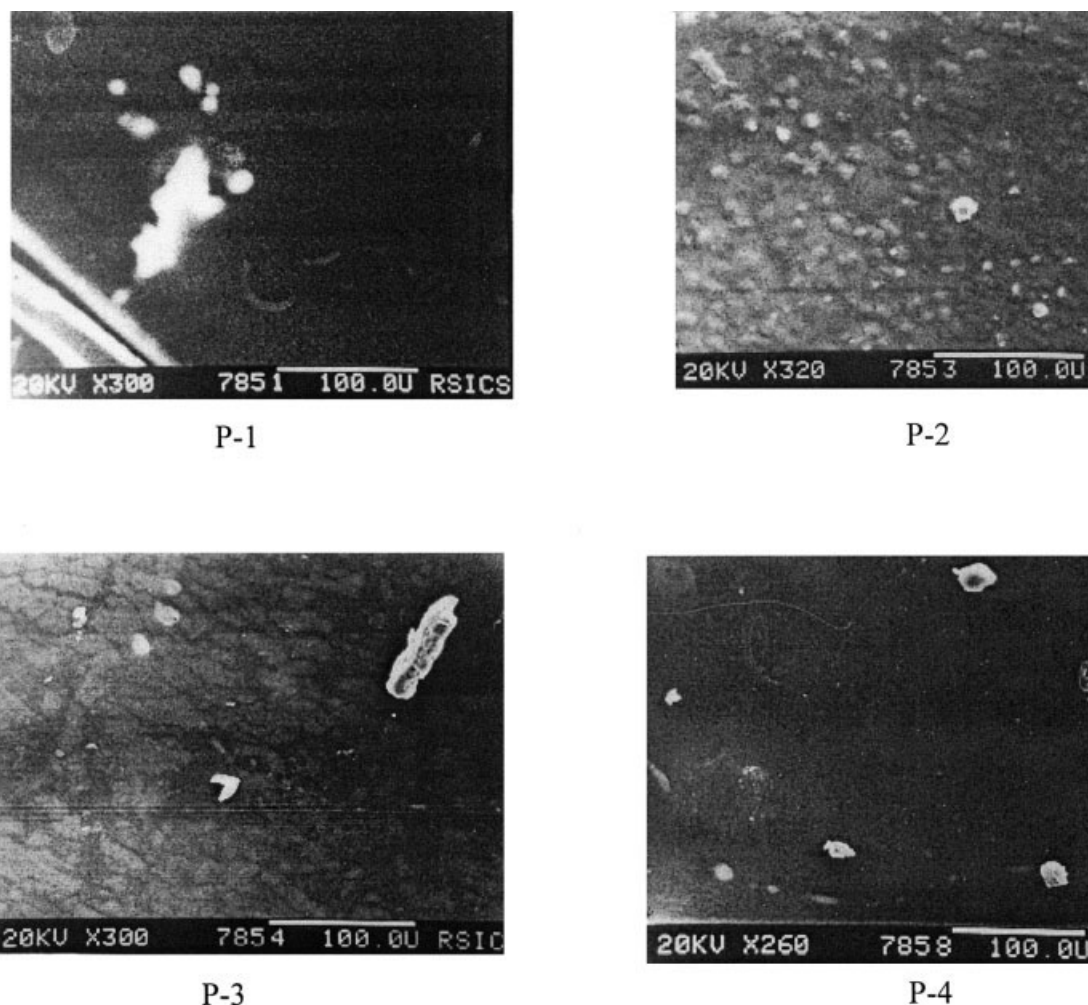| Polymer code	Alkyd resin (%)	Epoxy resin (%)
P-1	50 (Resin A)	50
P-2	50 (Resin B)	50
P-3	50 (Resin C)	50
P-4	—	100

Figure 1   SEM micrographs for the blends (P-1 to P-3) and amine-cured epoxy resin (P-4).

Among the SEM micrographs (Fig. 1), a blend containing an alkyd resin based on 100% PA (P-1) showed excellent dispersion in the epoxy resin. There was no observable phase separation in this blend. However, the addition of MA to the alkyd gave rise to phase separation [Fig. 1(P-2,P-3)]. Complete phase separation could be observed in the blend containing 50/50 PA/MA. The SEM study revealed that the addition of MA to the alkyd produced phase separation. In all cases, the haziness or turbidity was effectively eliminated by this solution-blending technique. Thus, the morphology of the solvent-cast films of the polymer blends depended on the composition of the blends, the nature of the solution, the rate of evaporation of the solvent, and the solution viscosity. However, the size of the domain of the disperse phase was largely governed by the level of polymer miscibility and the physical and chemical nature of the blend components. The domain reduction and relatively good interfacial adhesion of PA-based alkyd and epoxy resin blends [Fig. 1(P-1)] may be explained by the better compatibility of the aromatic moiety present in both

resins as well as polar–polar interactions between the π bonds of aromatic rings in both resins. In addition, the higher compatibility may be due to better interpenetrating network formation through the amine reaction of ester groups present in the PA-based alkyd resin along with normal crosslinking of hydroxyl or epoxy resins by the amine hardener.[1] There was a possibility of crosslinking by the hydroxyl groups of alkyd resins present in the fatty acid originally or generated during crosslinking reactions by the amine hardener with the epoxy groups of the epoxy resin in the presence of the amine hardener, which was also a base. Along with this, there was the possibility of hydrogen bonding between C=O of the acid of the alkyd resins with O—H of the epoxy resin present in the systems. All these phenomenon are shown in Scheme 1.

The better compatibility between the amine-cured epoxy and alkyd resin was further supported by FTIR studies. The FTIR studies of the blends (Fig. 2) indicated amide bond formation at 1747–1740 cm^{-1} between the ester of the alkyd and the amine hardener,[23]
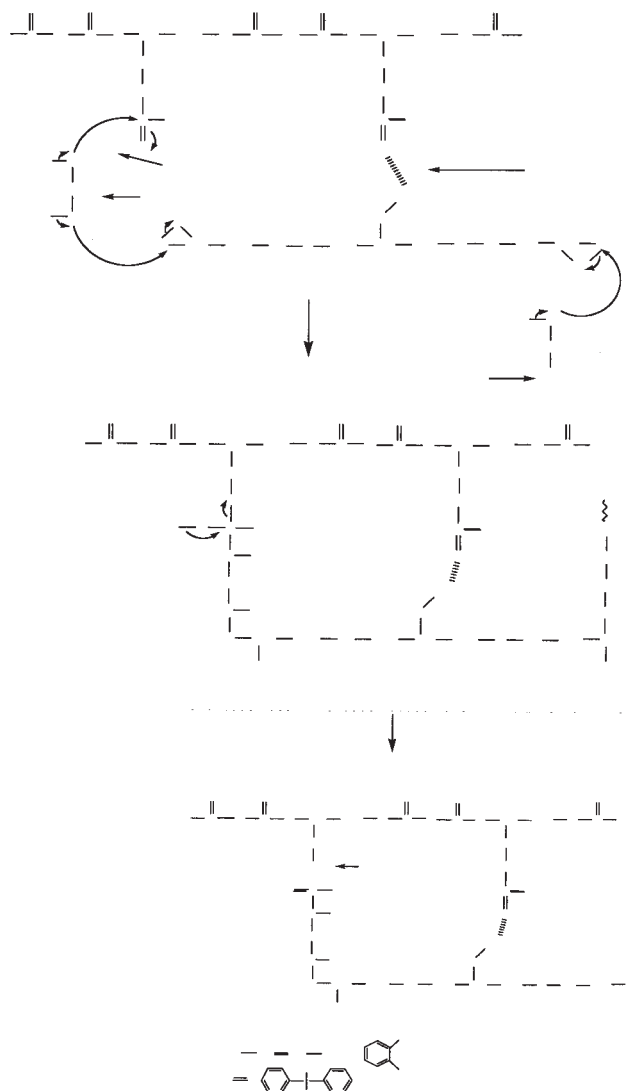
Scheme 1 Schematic representation of the phenomenon occurring during the crosslinking of the blend.

which was absent in the amine-cured epoxy resin. Thus, the amine hardener also acted as a compatibilizing agent for these blends. This was reflected in the performance of the blends in various properties.

Performances of the blends as coatings

In the process of drying, the coatings were converted from the liquid state to the solid state by the crosslinking reaction. In the case of only alkyd resins of nondrying oil, the crosslinking was mainly radical by peroxide or aerial oxidation via the absorption of oxygen from the atmosphere at a higher temperature. Therefore, it required a long time for hard drying. The drying time of all the alkyd resins improved significantly from several hours to several minutes (Table IV). This was due to a higher rate of curing of the epoxy resin by the amine hardener. There was a pos-

sibility of a chemical reaction of the epoxy resin with hydroxyl groups of the alkyd resin, in the presence of the amine hardener, along with the same type of reaction of the epoxy resin with amine groups of the hardener. However, with only peroxide used with cobalt octate, the blend could not be dried even after 8 h at 150°C. This may due to the fact that the epoxy resin remained totally uncured at that time, as no aerial oxidation or radical reaction was possible for the epoxy resins. Also, the reaction of the hydroxyl of the alkyd with the epoxy resin did not occur in this case under these conditions. With a combination of curing agents, that is, the systems used for individual alkyd and epoxy resins, the drying time was much higher (8–9 h) at 150°C. The blends were dried even without an amine hardener. However, the time for drying was long (7–8 h), and the temperature was high (~200°C).

Table IV shows that the hardness, as determined by different grade of pencils, of the blends was improved from individual alkyd resins, and this may be due to tighter and greater crosslinking of the epoxy resin. However, the improvement was more prominent for blend P-1, perhaps because of better compatibility, as supported by an SEM study and the presence of a rigid aromatic moiety in the matrix.
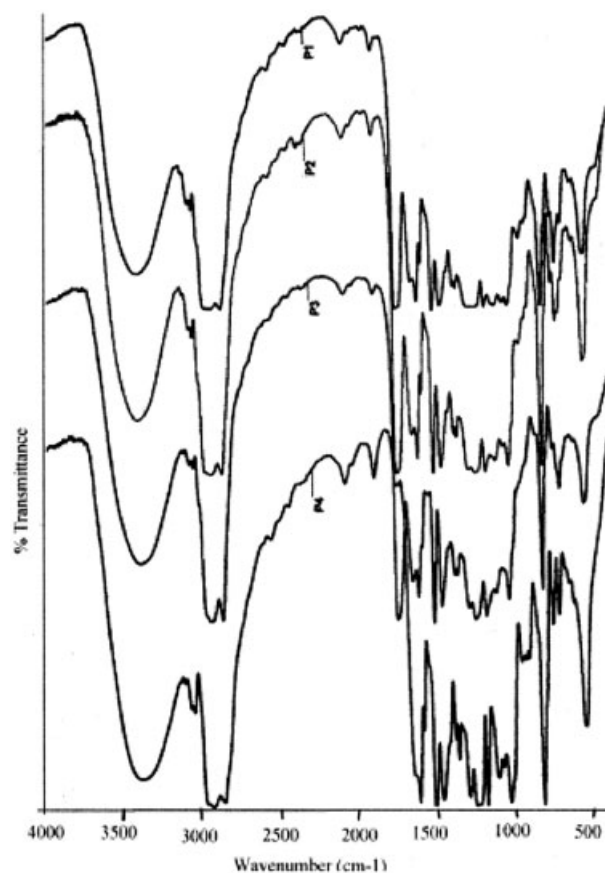

Figure 2 IR spectra for the blends (P-1 to P-3) and amine-cured epoxy resin (P-4).

TABLE IV
Performance Characteristics of R-1, R-2, R-3, P-1, P-2, P-3, and P-4

Polymer code	Drying time	Pressure test	Gloss (60°)	Flexibility	Pencil hardness	Adhesion (%)
R-1	9 h at 175°C[a]	P	85	P	H	100
R-2	7 h at 150°C[a]	P	81	P	HB	100
R-3	6 h at 150°C[a]	P	70	P	2B	100
P-1	55 min at 125°C	P	62	P	3H	100
P-2	45 min at 125°C	P	66	P	2H	100
P-3	40 min at 125°C	P	60	P	2H	100
P-4	30 min at 100°C	P	52	P	4H	100

[a] The individual alkyd resin was cured with accelerated peroxide curing system.[16]

Most of the light reflected from a coated surface is diffuse. Gloss refers to specular reflection or the light reflected at the same angle as the angle of incidence. The gloss of a coated surface depends on the amount of light absorbed or transmitted by the coating material, which is influenced by the smoothness or texture of the surface. In general, alkyds with long chains show semigloss, and this was observed in our case also (Table IV). The gloss of the alkyd resin was much higher than that of the epoxy resin only. Thus, the epoxy had low gloss characteristics that were improved via blending with the alkyd resins in all the cases (Table IV). This improvement may due to the better compatibility of these blends and good light stability of the alkyd resins for which the blends showed good gloss.

All the blends were tested for flexibility via the bending of a tin-coated panel at 180°, but no cracking, damage, or peeling was observed (Table IV). This indicated the excellent flexibility of the blends as well as the individual resins. This was mainly due to two factors: first, the nondrying oil acted as a permanent plasticizer,[24] and second, polyamidoamine imparted good flexibility.[25] The pressure test gave an idea about the impact resistance of the coated films. This study showed that both the blends and individual resins were sufficiently resistant to impact under the experimental conditions. This may have been due to the better flexibility of the alkyd resins, as supported by the flexibility test, as well as the good strength of the cured epoxy resin.

In general, the alkyd resins showed moderate adhesion, but the epoxy showed very good adhesion characteristics, as both of the resins had polar functional groups but epoxy had more polar groups. The results showed good adhesion for both the blends and the individual resins (Table IV).

The results of the chemical resistance are shown in Table V. Both the alkyd[16] and epoxy resins had good water and salt solution (aqueous NaCl solution) resistance, and so did the blends. The acid resistance of the individual alkyd resins and the blends was quite satisfactory, but the epoxy resin showed poor resistance to an acid solution (25% HCl). This may be due to the fact that the remaining epoxy groups in the epoxy resin were much more attracted toward the H$^+$ ion of the acid, and so the acid molecules penetrated the side of the coated sample. However, the alkali resistance of the blends improved to a significant extent because of the better alkali resistance of the epoxy resin. The individual alkyd resins[16] were easily affected by a 1% NaOH solution, whereas the blends showed relatively good resistance up to a 5% aqueous NaOH solution. The poor alkali resistance of the alkyd resins was due to the presence of alkali hydrolyzable ester bonds. However, in the blend, the epoxy component had good resistance to alkali because of the absence of any alkali hydrolyzable groups, and this also may have been due to the formation of some more alkali-resistant amide bonds through the carboxylic groups of alkyd with the amine groups of the hardener (Scheme 1). Among the blends, the blend P-1 showed relatively better alkali resistance, which was due to the presence of a more rigid aromatic moiety in the alkyd resin.[26]

Thermal study

Figure 3 shows that the blends had good thermal stability under the nitrogen atmosphere and that they started to degrade above 250°C. The same figure shows that the blends were degraded by a single-step pattern with char residues of 5, 2, 8, and 7% up to 600°C (for blends P-1, P-2, P-3, and P-4, respectively). However, the alkyd resins were less thermostable (<200°C) and started to degrade at approximately 200°C even for a PA-based alkyd in comparison with the epoxy resin, which started to degrade above 300°C (Fig. 3). This higher thermostability of the blends in

TABLE V
Chemical Resistance Test

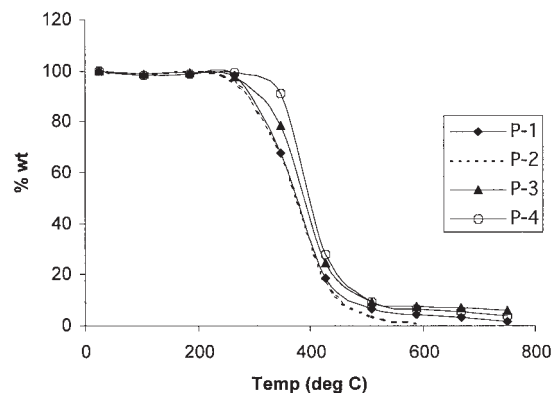| Type of medium	P-1	P-2	P-3	P-4
Alkali (5%)	Good	Peeled off	Peeled off	Excellent
HCl (25%)	Excellent	Excellent	Excellent	Good
NaCl (25%)	Excellent	Excellent	Excellent	Excellent
Distilled water	Excellent	Excellent	Excellent	Excellent

Figure 3 TGA traces for the blends (P-1 to P-3) and amine-cured epoxy resin (P-4).

comparison with the alkyd resins may be due to fact that there was some crosslinking between the free hydroxy groups present in the fatty acids of the oil originally or generated during the amine crosslinking reaction (Scheme 1) as well as better chemical interactions through hydrogen-bonding and polar–polar interactions. Thus, because of the better compatibility between the alkyd and epoxy resins, the thermostability of the blends was improved to a significant extent.

CONCLUSIONS

Blends of an alkyd resin based on nahar seed oil and an epoxy resin showed a significant improvement in the properties over those of the individual components. The properties, such as the drying time, pencil hardness, alkali resistance, and thermal stability, of the alkyd resins were improved via blending with the epoxy resin, whereas the acid resistance and gloss of the epoxy resin were improved via blending with the alkyd resins in all cases. This indicates that alkyd and epoxy resins have good compatibility and thus may be used as multipurpose coating materials.

References

1. Dieter, S. Paints, Coatings and Solvents, 1st ed.; VCH: New York, 1993.
2. Paul, S. Surface Coatings Science & Technology, 2nd ed.; Wiley: New York, 1997.
3. Athawale, V. D.; Joshi, K. R. Paintindia 2001, 51, 47.
4. Aigbodion, A. I.; Pillai, C. K. S.; Bakare, I. O.; Yahaya, L. E. Paintindia 2001, 51, 39.
5. Ronny, J. F. Off Dig Fed Soc Paint Technol 1964, 36, 32.
6. Narkhede, M. N. J Colour Soc 1991, 30, 2.
7. Abo, M.; Akira, M.; Mano, K.; Sakaguchi, K. Jpn. Pat. 7528986 (1975); Chem Abstr 1976, 84, 91810n.
8. Kokane, S. V. Paint India Annu 2002, 69.
9. Cesteros, L. C.; Isasi, J. R.; Katime, I. J Polym Sci Part B: Polym Phys 1994, 32, 223.
10. Ei Begawy, S. E. M.; Huglin, M. B. Eur Polym J 1991, 27, 1023.
11. Kim, B. K.; Oh, Y. S.; Lee, Y. M.; Yoon, L. K.; Lee, S. Polymer 2000, 41, 385.
12. Moltrasio, G. Eur. Pat. Appl. EP 432,480 (1991); Chem Abstr 1991, 115, 210284q.
13. Athawale, V. D.; Chamankar, A. V. Paint India Indian Paint Conference, Agra, India, Jan 17–19, 2003; Colour Publication Private Ltd: Mumbai, India, 2003 p 41.
14. Nakayama, Y. Prog Org Coat 1998, 33, 108.
15. Luttrull, D. K. U.S. Pat. 6,534,181 (2003).
16. Dutta, N.; Karak, N.; Dolui, S. K. Prog Org Coat 2004, 49, 146.
17. Methods of Sampling and Test for Paints, Varnishes and Related Products; Indian Standard 101, Part 5/Section 2, Clause 2; Indian Standards Institution; New Delhi, 1988.
18. Methods of Sampling and Test for Paints, Varnishes and Related Products; Indian Standard 101, Part 4/Section 4, Clause 2; Indian Standards Institution; New Delhi, 1988.
19. Methods of Sampling and Test for Paints, Varnishes and Related Products; Indian Standard 101, Part 5/Section 1, Clause 5; Indian Standards Institution; New Delhi, 1988.
20. Sarma, B.; Dolui, S. K.; Sarma, A. K. J Sci Ind Res 2001, 60, 153.
21. Annual Book of ASTM Standards; American Society for Testing Materials: Philadelphia, 1973.
22. Athawale, V. D.; Chamankar, A. I. http://www.coatings.de/articles/athawale/athawale.htm (accessed March 18, 2004).
23. Kemp, W. Organic Spectroscopy; Educational Low-Priced Books Scheme: London, 1991.
24. Payne, H. F. Organic Coating Technology; Wiley: New York, 1954; Vol. 1.
25. Oil and Colour Chemist's Association of Australia. Surface Coatings; Chapman & Hall: London, 1981; Vol. 1.
26. Aigbodion, A. I.; Okeimen, F. E.; Obazee, E. O.; Bakare, I. O. Prog Org Coat 2003, 46, 28.